Chemical Studies of the Western Pacific Ocean. II. The Chemical Composition of the Oceanic Salt. Part 2.*

By Yasuo MIYAKE.

(Received January 9, 1939.)

Methods of Analysis (*Continued*). *Strontium.* It is but lately that strontium was found to be the fifth in abundance among the metallic elements in sea water. Desgrez and Meunier[1] determined strontium in the waters of the English Channel by the spectroscopic method, in which the intensity of strontium line 4607 Å was compared with the reference line 4427 Å of iron. They obtained the result that the channel water contains 13.5 mg. of strontium per litre. T. G. Thompson and B. D. Thomas,[2] who recently repeated the spectroscopic analysis, ascertained the value of Desgrez and Meunier for this element.

It is interesting that the ratio of strontium to calcium in sea water is 0.033, which is considerably higher than the ratio 0.0059, calculated from the Clarke number. As has been discussed by H. Wattenberg,[3] this discrepancy is probably due to the difference in the solubilities of calcium carbonate and strontium carbonate. Since these determinations were both made spectroscopically, the present author attempted a gravimetric analysis of the element. The separation of this small amount of strontium from calcium is, of course, a rather difficult task. R. Fresenius' method[4] of separation, in which the nitrate of both elements are swirled in a mixture of alcohol and ether, was adopted. Since calcium nitrate is about 160 times more soluble than strontium nitrate in a mixture of equal volumes of absolute alcohol and absolute ether, strontium nitrate remains insoluble. 1000 c.c. of sea water, to which ammonium chloride containing little ammonia had been added, was heated to boiling and a sufficient quantity of ammonium oxalate was poured to precipitate calcium and strontium completely. The filtrate was examined if any calcium was present. The precipitation was repeated several times in order to remove magnesium as completely as possible. The oxalates of calcium and strontium were converted by ignition into oxides, and then dissolved in dilute nitric acid, evaporated to dryness on a water bath and finally dried completely in an air bath at above 130°C. The procedure of separation, hereafter, was carried on with alcohol and ether according to the direction of Hillebrand and Lundell. The separation was repeated twice and a very small quantity of undissolved strontium nitrate was filtered off on a small filter paper and ignited to a constant weight.

From this gravimetrical result, the content of strontium in the sea water of the Pacific Ocean near Japan has been found to be 14.4 mg. per

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* Part 1: this volume, 29.

(1) A. Desgrez and J. Meunier, *Compt. rend.*, **183** (1926), 689.

(2) *Bull. Nat. Research Council*, **85** (1932), 95.

(3) H. Wattenberg, *Z. anorg. allgem. Chem.*, **236** (1938), 339.

(4) Hillebrand and Lundell, "Applied Inorganic Analysis," 490, New York (1929).

litre, which is almost of the same order in amount in values as the results from the spectroscopic method. The slight difference between the two methods is unavoidable because of the inherent difficulties of the analytical processes.

Boron. After the geochemical studies of boron had been published by V. M. Goldschmidt and Cl. Peters,[5] the boric acid content in sea water became one of the most interesting subject in oceanographical chemistry. V. M. Goldschmidt and his collaborator determined precisely the boron content in various earth crust forming materials by the spectroscopic method. Thereby, they obtained the result that sea water contains 30 mg. of B_2O_3 per litre, a value considerably larger than L. Dieulafait's[6] old data. According to L. Dieulafait's determination, which is frequently referred to in text-books of oceanography, the quantity of boron in sea water has been estimated to be at least 0.2 mg. per litre. As H. Wattenberg[3] stated in his recent paper, this is one of the few cases, where the older analyses gave a value too low for the rarer elements in the sea water.

Immediately after the investigation of Goldschmidt and Peters, H. Wattenberg[7] tried to ascertain the boric acid content in sea water by the direct titration method, using mannitol and a sodium hydroxide solution. He obtained by this method quite easily 15.6 mg. and 16.1 mg. of B_2O_3 per litre, which are in good agreement in the order of the magnitude with Goldschmidt's value. At the same time, independently of H. Wattenberg, E. G. Moberg and M. W. Harding[8] of the Scripps Institute obtained almost the same result. If these higher values are correct, then besides carbonic acid, boric acid must be taken into consideration in the acid-base equilibrium in sea water. So K. Buch,[9] using the data of the above mentioned authors and the one obtained by himself, calculated theoretically the influence of the boric acid upon the *p*H value of sea water; at the same time, he gave the chlorinity ratio of boron in sea water, which seemed to be almost constant and expressible by the following formula:

$$B‰ = 0.00023 \sim 0.00025 \times Cl‰$$

Now, an attempt was made to determine the boric acid content in waters of the Pacific Ocean near Japan by the gravimetric methods inasmuch as all of the former values had been obtained either spectrographically or volumetrically.

At first Gooch and Jones' method has been tried. It determines boron gravimetrically as calcium borate, after the extraction of the borate with ethyl alcohol and expelling it as a methyl ester. A 1000 c.c. portion of sea water, was evaporated to dryness, and then methyl alcohol was added, followed by an extraction overnight.

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(5) V.M. Goldschmidt and Cl. Peters, *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, **1932**, 402, 528.
(6) L. Dieulafait, *Compt. rend.*, **85** (1877), 1352.
(7) H. Wattenberg, "Wiss. Ergeb. Meteor-Exp.," VIII, 132, Berlin (1933).
(8) E.G. Moberg and M.W. Harding, *Science*, **77** (1933), 510.
(9) K. Buch, *J. conseil intern. exploration mer*, **8** (1933), 309.

With all the scrupulous care, the results obtained were always too low, when compared with the former values. By this method, there could not be obtained a value higher than 1.2 mg. of H_3BO_3 per litre. The second method adopted was Chapin's procedure, in which boric acid in sea salt is expelled directly with the vapour of methyl alcohol, thus forming a methyl ester of boric acid, which is converted to calcium borate. As by Jones and Gooch's method, values so high as the titrimetric ones could not be obtained by this method. The maximum value was 7.3 mg. of H_3BO_3 per litre.

In both of these cases, the chief sources of failure lay probably in the difficulty in extracting or expelling the small amount of boric acid from so large a bulk of other salts. After several trials had been in vain, the original plan of gravimetric determination was given up and the method of direct titration of sea water was adopted by modifying H. Wattenberg's procedure at a few points.

To a 100 c.c. portion of sea water, a slight excess of hydrochloric acid solution was added and after heating under suction to remove carbon dioxide completely, the excess of hydrochloric acid was cautiously titrated with a solution of sodium hydroxide using *p*-nitrophenol as the indicator. Then a small quantity of mannitol was added to produce free acid which was titrated with a 0.1 or 0.05 N solution of sodium hydroxide (the indicator, phenolphthalein).

Also invert sugar was used in place of mannitol, as recommended by I. M. Kolthoff.[10] The values of both procedures were in good agreement with those of Wattenberg and others. The results are given in Table 1.

Table 1.

Position		Chlorinity	B (mg./l.)	B (‰)/Cl (‰)
Lat. N	Long. E			
36°14′	141°26′	19.24	4.73	0.000246
38°22′	142°35′	18.76	4.73	0.000252

The chlorinity ratios of boron here obtained were almost the same as the upper limit of the values calculated by K. Buch. To eliminate the influences of other salts, known quantities of boric acid were added to the sea water and titrated as usual, the results were completely additive. Recently I. Igelsrud, T. G. Thompson, and B. M. G. Zwicker[11] determined the boron content in sea water on 377 samples from the coastal waters of the Northeastern Pacific. They obtained the result that the average boron-chlorinity ratio is 0.0223 (this is not the ratio of the number of promille boron to the chlorinity as described above, but the value milligram atom boron divided by the chlorinity). When compared with this average, the boron-chlorinity ratio obtained by the author seems to be

(10) I.M. Kolthoff, "Die Massanalyse," 119, Berlin (1928).
(11) I. Igelsrud, T.G. Thompson, and B.M.G. Zwicker, *Am. J. Sci.*, [5], **35** (1938), 47.

slightly larger (0.0228, 0.0234). A further quantitative discussion will be done in future.

Summary.

(1) Strontium in sea water from the Western Pacific Ocean has been determined gravimetrically; the analytical result: 14.4 mg. Sr per litre.

(2) Boron in sea water has been determined volumetrically; the analytical result: 4.73 mg. B per litre.

The author wishes to express his hearty thanks to Prof. T. Okada, Director of the Central Meteorological Observatory of Japan, for his kind guidance and the permission of publishing this report. He is also indebted to Mr. H. Matui for his assistance in the analytical work.

The Central Meteorological Observatory of Japan.

Chemical Studies of the Western Pacific Ocean. III. Freezing Point, Osmotic Pressure, Boiling Point and Vapour Pressure of Sea Water.

By Yasuo MIYAKE.

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Freezing Point. The freezing point of sea water was measured by Knudsen and Hansen[1] in 1903, and it is expressed by the following empirical formula:

$$\tau = -0.0086 - 0.064633\ \sigma_0 - 0.0001055\ \sigma_0^2$$

where τ is the freezing point, and $\sigma_0 = (S_0 - 1) \times 1000$, in which S_0 represents the specific gravity of sea water at 0°C. with reference to distilled water at 4°C. The relation between the freezing point and chlorinity,

$$\tau = -0.0966\ \mathrm{Cl} - 0.00000520\ \mathrm{Cl}^3$$

was derived by B. D. Thomas[2] from Knudsen-Hansen's formula. The present author has repeated the measurement of the freezing point of sea water and obtained a new empirical formula which seems to be more adequate than the former equations.

(1) O. Krümmel, "Handbuch der Ozeanographie," Band 1, 240, Stuttgart (1907).
(2) *Bull. Nat. Research Council*, **85** (1932), 84.

Experimental. Sea water of known chlorinity was diluted with water into six samples. The chlorinity, the position, the depth and the date of collection of the original sea water are as follows: Cl, 18.54‰; N 39°46′, E 143°16′; 145 m.; March 17th, 1938. The measurements were made by the ordinary method. Into a beaker containing about 100 c.c. of sample water, a Beckmann's thermometer and a certified stem thermometer (−20°～50°C.) were inserted and the content was cooled indirectly with a cooling mixture under incessant stirring. The temperature of the water, taken at intervals of thirty seconds, was plotted giving the cooling curve. The freezing point was determined from the tangent of the curve after the state of supercooling was broken. At first, the freezing point of distilled water was carefully measured and the reading was used as a reference standard. The difference between the reading of a sample and that of the standard directly gives the depression ΔT of the freezing point of sea water.

Results of the Measurements. The results of the measurements are given in Table 1.

Table 1.

Cl (‰)	Salinity (‰)	Depression of the Freezing Point, ΔT
18.54	33.49	1.895
13.07	23.62	1.350
9.37	16.94	0.970
7.53	13.62	0.770
4.75	8.60	0.495
1.90	3.46	0.195

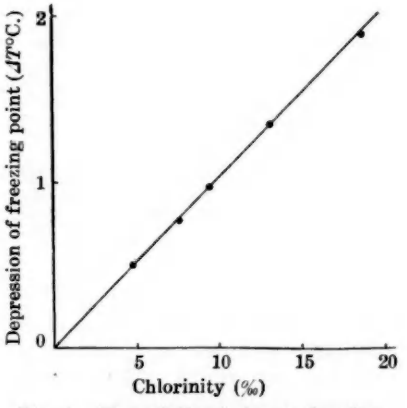


Fig. 1. The relation between freezing point depression and chlorinity.

As shown in Fig. 1, the relation between the chlorinity and the freezing point depression is almost linear and may be represented by the following simple formula:

$$\Delta T = 0.102710\ \mathrm{Cl}.$$

A Comparison of Author's Formula with Knudsen-Hansen's Equation. The freezing point of sea water of various chlorinities was next measured. The results have been compared with the values calculated from the equation of Knudsen-Hansen and from the new formula. From the experimental results shown in Table 2, we can see that the values obtained by the present formula are in good agreement with the measurements, the average deviation between them being only $\pm 0.005_5$°C.; on the other hand, the values calculated from Knudsen-Hansen's formula constantly show a deviation of about 0.08°C, giving values that are too high. The comparison shows clearly that the new formula is superior to Knudsen-Hansen's formula.

Table 2.

Chlorinity	ΔT, observed	ΔT, calculated by the new formula	ΔT, calculated by Knudsen's formula
18.22	1.875	1.872	1.792
18.28	1.875	1.878	1.798
18.42	1.900	1.892	1.812
18.48	1.890	1.898	1.819
18.57	1.915	1.907	1.828
18.59	1.915	1.909	1.830
18.60	1.915	1.910	1.831
18.75	1.935	1.926	1.846
19.38*	1.985	1.991	1.911
19.39**	1.990	1.992	1.912

* The standard water supplied by the Imperial Fisheries Experimental Station, Japan.

** The standard water supplied by Prof. Knudsen.

The Calculation of the Osmotic Pressure of Sea Water. When the depression of the freezing point of a solution is known, its osmotic pressure can readily be estimated. The theoretical relation between osmotic pressure and freezing point depression is given by the next formula:

$$P_0 = \frac{41.35\ r\ \delta}{T_0}\ \Delta T(\text{atm.})$$

where P_0 is the osmotic pressure at 0°C.; r, the heat of fusion of water, 79.65 cal.; δ, the density of water at 0°C.; ΔT, the freezing point depression. Substituting numerical values in the formula, we obtain the simple equation:

$$P_0 = 12.06 \times \Delta T.$$

In Table 3, the osmotic pressure corresponding to various chlorinity values, calculated by the above formula with additional correction for the heat of solution, are given. The empirical relation between osmotic pressure, chlorinity and temperature is represented by the following equation:

$$P_t = 1.240\ \text{Cl} + 0.00454\ \text{Cl} \cdot t.$$

Table 3.

Cl (‰)	ΔT	P_0 (atm.)	Cl (‰)	ΔT	P_0 (atm.)
1	0.103	1.24	12	1.233	14.88
2	0.205	2.47	13	1.335	16.12
3	0.308	3.71	14	1.438	17.36
4	0.411	4.96	15	1.541	18.60
5	0.514	6.20	16	1.643	19.83
6	0.616	7.43	17	1.746	21.09
7	0.719	8.67	18	1.849	22.34
8	0.822	9.91	19	1.951	23.58
9	0.924	11.15	20	2.054	24.82
10	1.027	12.40	21	2.157	26.07
11	1.130	13.64	22	2.260	27.31

When the temperature is constant, the osmotic pressure increases by 1.24 atm. per unit increase in chlorinity. In Table 4 and Fig. 2, the osmotic pressures at 0°C. calculated by author's formula are compared with those by Krümmel and Stenius.[1] Here the concentration of sea salt is expressed in terms of salinity instead of chlorinity. As seen in this table and Fig. 2, author's values for the osmotic pressure are slightly larger than those of Krümmel and Stenius.

Table 4. Osmotic pressure of sea water at 0°C. (atm.)

Salinity (‰)	Krümmel-Stenius	Miyake
5	3.23	3.41
10	6.44	6.84
15	9.69	10.28
20	12.98	13.72
25	16.32	17.16
30	19.67	20.59
35	23.12	24.05
40	26.59	27.49

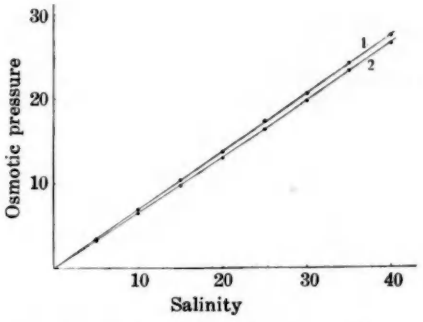


Fig. 2. The relation between osmotic pressure and salinity.
1: Miyake. 2: Krümmel-Stenius.

The Calculation of the Boiling Point Elevation. If we know the osmotic pressure of sea water, then we can estimate the boiling point elevation by the following equation:

$$P = \frac{41.35\ l\ \delta}{T}\ \Delta T,$$

where l is the heat of evaporation of water, i.e. 536.6 cal.

But, $$P = P_0\{1-0.00366(T-T_0)\}$$

Therefore, $$\Delta T = 0.02397\ P_0\ .$$

The numerical values calculated by this equation are shown in Table 5, where the results are compared with Krümmel's data.[1]

Table 5. Boiling point elevation of sea water. ΔT°C.

Salinity (‰)	5	10	15	20	25	30	35	40
Miyake	0.08	0.16	0.25	0.33	0.41	0.49	0.58	0.66
Krümmel	0.08	0.16	0.23	0.31	0.39	0.47	0.56	0.64

The experimental formula between the salinity and the boiling point elevation may be expressed as follows:

$$\Delta T = 0.01645\,S. \qquad S: \text{the salinity.}$$

The Depression of the Vapour Pressure. We can easily calculate the vapour pressure depression for sea water at its boiling point when the boiling point elevation is known. There are two means of calculating the depression of the vapour pressure, i.e., one is from the pressure of saturated water vapour near 100°C. under the pressure of 760 mm. Hg (1); and the other is from the boiling point data of water at pressures slightly lower than 760 mm. Hg (2). These data have been quoted from Landolt-Börnstein's Tables, and the results of the calculation are as follows:

Table 6. The depression of the vapour pressure. (mm. Hg)

Salinity (‰)	5	10	15	20	25	30	35	40
From (1)	2.17	4.34	6.76	8.91	11.07	13.21	15.60	17.75
From (2)	2.17	4.33	6.77	8.93	11.07	13.20	15.62	17.75
Average	2.17	4.33_5	6.76_5	8.92	11.07	13.20_5	15.61	17.75
Krümmel	2.13	4.23	6.45	8.47	10.73	12.97	15.23	17.55

Summary.

(1) The freezing point of sea water from the Western Pacific Ocean has been measured and a new empirical formula for the relation between freezing point and chlorinity has been obtained, which seems to be more adequate than Knudsen-Hansen's equation.

(2) The osmotic pressure, the boiling point elevation and the depression of the vapour pressure of sea water have been calculated.

The author wishes to express his hearty thanks to Prof. T. Okada, Director of the Central Meteorological Observatory of Japan, for his kind guidance and the permission of publishing this report. He is also indebted to Mr. H. Matui for his earnest assistance throughout this work.

The Central Meteorological Observatory of Japan.

On the Nature of Foam. IV. Phase Inversion and Foaming of Emulsion Consisting of Acetic Acid, Ethyl Ether and Water.

By Tunetaka SASAKI.

(Received February 10, 1939.)

It was reported in the preceding paper,[1] that the heterogeneous region of the system consisting of acetic acid, ethyl ether and water (AEW-system) is divided into two parts, namely, foamy and non foamy region. It was discovered, by a more detailed observation, that between these foamy and non foamy regions, there exist some system in which foam is produced by a certain mode of shaking, while it is not produced by another mode of shaking. Moreover, the type of emulsion is different in each of the above two cases. Present paper describes such phase inversion of AEW-emulsion produced by shakings and its influence upon the foam formation.

Experiments.

I. Foam-Nonfoam System.[2] We take a certain composition of AEW-system, for example, the system consisting of 2.33 c.c. of acetic acid, 3.79 c.c. of ethyl ether and 3.88 c.c. of water which corresponds to the point (a) in the mutual solubility diagram of AEW-system as shown in Fig. 1, and shake in a test tube. Then, the following two cases are observed according to two different modes of shaking.

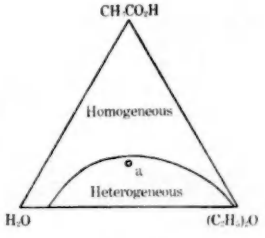


Fig. 1.

(1) The test tube is held vertically by hand, shaken up and down several times strongly in the usual manner, and then left at rest. In this case the formation of emulsion was observed without any indication of the foam formation.

(2) At first, the upper portion of the test tube is held and the lower portion is made to swing forwards and backwards until considerable amounts of upper and lower liquids are mixed together, then, the usual up-and-down shaking as in (1) is made and emulsification is completed. Observation after shaking shows the foam formation in the resulting emulsion.

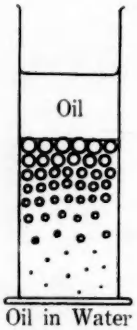
II. Mode of Shaking and Emulsion Type. The results of section (I) show, that a certain system of AEW foams or does not foam according to the different modes of shaking. Such phenomena have not been observed up to the present. To investigate these phenomena more precisely, we have made close observations to the two emulsions obtained in (1) and (2) of section (I).

(1) Sasaki, this Bulletin, **13** (1938), 669.
(2) The term is used for such a system as shown in this section.

These emulsions are both unstable, their disperse phases consisting of comparatively large liquid drops. It may be called mechanical suspension rather than true emulsion. When we trace, however, the process of breaking up these two emulsions, following differences are observed between them.

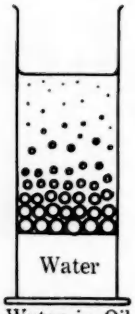
(1) In emulsion which is described in (1) of section (I), it can clearly be observed with naked eyes, that emulsion droplets move upwards in the dispersing medium increasing their size as they go up, and at the top of emulsion, in the course of time, they are separated from the dispersing medium as a transparent liquid layer upon the bulk. Thus, emulsion finally breaks up perfectly into two transparent liquid layers. Fig. 2 shows these behaviours.

(2) In emulsion which is described in (2) of section (I), the appearance is just reverse. Emulsion droplets sink in the dispersing medium, they grow in their size as they go down, and in the course of time they are separated, at the bottom, from the dispersing medium into transparent layer. The emulsion finally breaks up into two layers. These relations are also shown in Fig. 3.



Oil in Water

Fig. 2.



Water in Oil

Fig. 3.

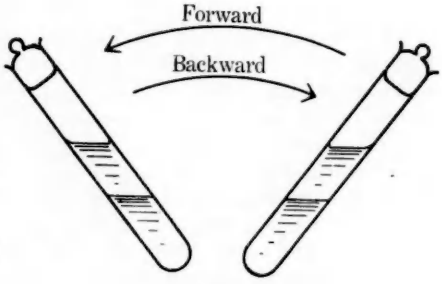


Fig. 4.

It is concluded from the above observations, that in the case of emulsion (1) or Fig. 2, the upper layer of original heterogeneous system is dispersed in the lower one. It may be called oil-in-water (O-in-W) emulsion, as the upper layer mainly consists of ethyl ether which is insoluble in the lower layer of aqueous mixture. In the case of emulsion (2) or Fig. 3, on the contrary, the lower layer of original system is dispersed in the upper one, or it may be called water-in-oil (W-in-O) emulsion. Thus, it is evident that in a certain composition of AEW-system, the mode of shaking described in (1) of section (I) favours the emulsification of oil in water which does not foam, while another mode of shaking as described in (2) of section (I) favours the emulsification of water in oil which foams. The foam formation of this system will be discussed later.

Further experiments show that the formation of O-in-W emulsion is still more facilitated by shaking a test tube in the following manner. The lower part of the test tube is held by hand and the upper portion is shaken with forward and backward motion, which is better described as a jerk. It is illustrated in Fig. 4.

III. Heterogeneous Region and Emulsion Type. As it is evident, that emulsion type is affected by the mode of shaking, we subsequently made experiments to examine how the type of emulsion of heterogeneous AEW-system is influenced by these two modes of shaking.

For this purpose, we take a constant volume of a system belonging to the heterogeneous region of AEW, and is shaken in a test tube by the following two manners.

(1) The test tube is shaken several times as shown in Fig. 4, and then, it is shaken up and down as in usual manner.

(2) The test tube is shaken in the same manner as described in (2) of section (I).

After shaking, the test tube is left at rest in vertical position, and the behaviour of breaking up of emulsion is observed. The following results have been obtained.

In the region where the volume of the upper layer is in excess compared with that of the lower one, emulsion is obtained in which the lower layer is dispersed in the upper one, i.e. W-in-O emulsion, no matter what the modes of shaking. Such a region is shown as A in Fig. 5. On the contrary, in the region where volume of the lower layer is in excess compared with that of the upper one, the upper layer is dispersed in the lower one, i.e. O-in-W emulsion is obtained, independent of the modes of shaking. This region corresponds to B in Fig. 5.

Now, between these A and B region, a narrow zone has been discovered in which a system changes its type of emulsion according to the above two modes of shaking. This is considered to be the zone of phase inversion by shaking. Observed systems belonging to this zone are shown in Table 1. These systems become O-in-W emulsion by the shaking of the mode (1), while they become W-in-O emulsion by the shaking of the mode (2). Plotting the points corresponding to these compositions on Fig. 5 (indicated by circlets), the line PQ is obtained. Although the shape of this phase inversion zone was not determined distinctly, it is considered to be a narrow region including the line PQ.

Table 1.

Volume composition of phase inversion system (c.c.)		
Acetic acid	Ethyl ether	Water
0	3.75	6.25
0.43	3.90	5.67
0.95	3.81	5.24
1.51	3.54	4.95
2.10	3.70	4.20
2.40	3.80	3.80

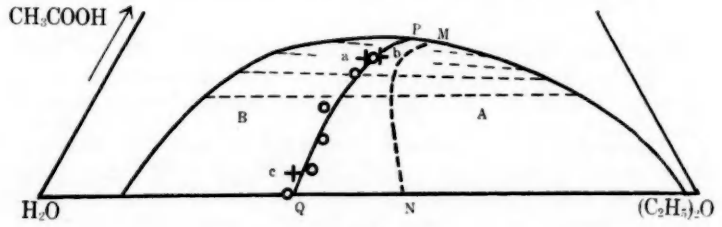


Fig. 5.

IV. Zone of Phase Inversion. In order to investigate this zone of phase inversion more precisely, we carried out, further, the following experiments.

We take systems belonging to this zone, namely, in the vicinity of the line PQ, and applied to them the following modes of shaking.

(1) The mode of shaking as shown in (1) of section (III) or the following method is employed which gives the same effect. The test tube is supported vertically, pulled upwards quickly and then brought down slowly. After repeating these motions several times, it is shaken up and down as in the usual manner.

(2) The mode of shaking as shown in (2) of section (III) is also adopted here.

(3) The test tube is simply shaken up and down as in the usual manner, from the beginning.

Up-and-down shaking involved in the above three modes of shaking is performed by the same shaking apparatus and in the same condition as described in the preceding paper[1] (50 vibrations for 10 seconds with amplitude of 12 cm.). Various quantities are measured for emulsion thus produced which are shown in Table 2. In this table, stability of

Table 2.

System	Composition in volume (c.c.)			Mode of shaking			Volume ratio	
	Acetic acid	Ethyl ether	Water	(1)	(2)	(3)	Upper layer	Lower layer
(a)	2.33	3.79	3.88	O-in-W $S_e = 24$ $S_f = 0$ $H = 0$	W-in-O $S_e = 41$ $S_f = 1.5$ $H = 0.6$	O-in-W same as (1)	0.66	1.00
(b)	2.40	3.90	3.70	O-in-W $S_e = 28$ $S_f = 0$ $H = 0$	W-in-O $S_e = 44$ $S_f = 1.7$ $H = 0.5$	W-in-O same as (2)	0.72	1.00
(c)	0.38	3.66	5.96	O-in-W $S_e = 10$ $S_f = 0$ $H = 0$	W-in-O $S_e = 12.5$ $S_f = 0$ $H = 0$	O-in-W or W-in-O	0.45	1.00

S_e and S_f denote stabilities of emulsion and foam in second respectively; H, height of foam zone in cm.

emulsion or foam is expressed by time required from immediately after shaking to the complete collapse of emulsion droplets or foam zone, respectively. Height of foam zone is also measured soon after shaking.

V. Discussion. First of all, the experiments of section (I) show, that there exists a system of certain composition which can behave both foamy and non foamy, according to the modes of shaking. It is expected, that such difference in the foam formation is necessarily ascribed to the difference in the nature of emulsions in which these phenomena are

taking place. In fact, it is confirmed, as described in section (II), that the foamy emulsion is W-in-O type (Fig. 3), while the non foamy emulsion is O-in-W one (Fig. 2). Thus, the phenomena of foam formation of such systems are closely related to the type of emulsion or the possibility of phase inversion which is caused especially by the mode of shaking.

Now. it is worth while to give a glance to the theories of type determination or phase inversion of emulsion.

The type of emulsion is generally considered to be determined by the nature of emulsifying agent. Bancroft[3] considered, that the interfacial tension between emulsifying agent and water or oil plays an important rôle and liquid which constitutes an interface of smaller interfacial tension forms a dispersing medium. Langmuir,[4] Harkins[4] and Hildebrand[4] indicated the relation between the type of emulsion and the molecular shape of emulsifying agent, which enables the explanation of the facts, that Na-soap favours the emulsification of O-in-W type, while Mg- or Al-soap favours that of W-in-O type. The phenomena of phase inversion are also influenced by above conditions. Clowes[5] succeeded to invert O-in-W emulsion stabilized by Na-oleate into W-in-O emulsion by adding Ca-salt to it. Bhatnagar[6] studied the effect of added electrolyte to the type or phase inversion of emulsion. Parsons and Wilson[7] also made the systematic investigation upon these lines.

Now, all these explanations assume the existence of the emulsifying agent of definite kind and its selective determination of type of emulsion. The emulsifying agent stabilizes one type of emulsion selectively to the opposite one. Above explanation, however, cannot be applied in the case where it is difficult to determine which of the liquid components is an emulsifying agent. It may be emphasized, that in these systems which belong to mechanical suspension rather than true emulsion, the readiness or tendency with which certain type of emulsion is produced, is the different matter from the stability of emulsion thus produced, as can be seen in the later part of this paper. Both of these factors are generally involved in all above theories and it is interesting to find the analogy between these relations and the suggestion made by Foulk[8] upon the mechanism of foam formation. The tendency of establishing either type of emulsion is sometimes confused with the stability. We, further, consider the cases where the effects of the other factors than the stability are predominant.

Briggs[9] noted, that a certain type of emulsion are quickly produced by the method of intermittent shaking. It is frequently experienced, that the emulsification is facilitated by adding the disperse phase little by little and not all at once. Wa. Ostwald[10] discussed the influence of volume ratio of two liquid components upon the type of emulsion and

(3) Bancroft, *J. Phys. Chem.*, **17** (1913), 501.
(4) Langmuir, *J. Am. Chem. Soc.*, **39** (1917), 1848; Harkins and co-workers, *ibid.*, **39** (1917), 354, 541; Finkle, Draper, and Hildebrand, *ibid.*, **45** (1923), 2780.
(5) Clowes, *J. Phys. Chem.*, **20** (1916), 407.
(6) Bhatnagar, *J. Chem. Soc.*, **117** (1920), 542; **119** (1921), 61, 1760.
(7) Parsons and Wilson, *Ind. Eng. Chem.*, **13** (1921), 1116.
(8) Foulk, *Ind. Eng. Chem.*, **21** (1929), 815.
(9) Briggs, *J. Phys. Chem.*, **24** (1920), 120.
(10) Wa. Ostwald, *Kolloid-Z.*, **6** (1910), 103.

indicated the critical volume ratio at which the system undergoes phase inversion. Robertson[11] and Bhatnagar[6] also observed the same effect. Ostwald[10] further pointed out another possibility, that the emulsion type is determined by the influence depending upon whether the glass surface of the vessel is wetted with oil or water previous to making emulsion and said, that in certain system of two liquids, the poorer wetting liquid will be emulsified in the better one. Although these factors are overshadowed in its determining effect by the nature of the emulsifying agent, as discussed by Briggs and Schmidt,[12] they have considerable effects in the case of unstable and coarser mechanical suspensions with no emulsifying agent specified.[6] These factors rather affect the process of establishment of emulsion type, and not the stability of emulsion produced. The mode of shaking discussed in this paper is also considered to be one of these factors where the emulsifying agent has little significance.

It is described in section (III), that the heterogeneous region of AEW-system is divided into three parts, referring to the type of emulsion, as shown in Fig. 5. The region A of this diagram mainly consists of systems having fairly larger volume of an upper layer (V_u) than that of a lower one (V_l). Such a system shows the tendency of the lower layer being dispersed in the upper one, namely, W-in-O emulsion, no matter what the mode of shaking. This tendency seems to be determined mainly by the ratio $V_u:V_l$ as suggested by Bhatnagar[6] and Robertson,[11] namely, in case where there is marked difference in volume between two layers, liquid of larger volume shows the tendency of becoming a dispersing medium, and this tendency is more remarkable as the difference in volume grows larger. In the region B, the relation is reverse. Here V_l is markedly larger than V_u, and the system of this region shows the tendency of the upper layer being dispersed in the lower one, namely, O-in-W emulsion results, independent of the mode of shaking.

It is interesting to note, that the region A contains a system in which V_u is smaller than V_l and yet the upper layer becomes a dispersing medium on shaking. This suggests that some other factors, in addition to volume ratio, influence the tendency in establishing an emulsion type. Specific action of interface, for example, can be considered.

Phase inversion zone, namely, the region in which a system shows the tendency of producing both types of emulsions according to the mode of shaking, is situated along PQ line in Fig. 5. Such possibility of forming two types of emulsions from one and the same system was once pointed out by Ostwald.[10] Woodman[13] studied the system of cresylic acid–gelatine–water, and observed that, in certain case, both types of emulsions are possible, depending mainly upon the mode of shaking. The fact was confirmed distinctly in the present experiments.

When we trace the locus of middle points of tie-lines (i.e. points corresponding to the system in which $V_u = V_l$), dotted line MN is obtained in Fig. 5. Now, if the emulsion type is determined by the volume ratio

(11) Robertson, *Kolloid-Z.*, **7** (1910), 7.
(12) Briggs and Schmidt, *J. Phys. Chem.*, **19** (1915), 478.
(13) Woodman, *J. Phys. Chem.*, **30** (1926), 658.

of two liquids alone, phase inversion zone is reduced to the line PQ which must coincide to the line MN. In practice, phase inversion zone has a narrow area instead of a line, and does not coincide to the line MN which is situated in the region A, as shown in Fig. 5. This means, that the position of the phase inversion zone cannot be determined by volume ratio alone, and also indicates the influences of some other factors. The specific action, at the interface, of acetic acid is quoted for example. It is clear, that in regions A and B, the influence of relative volume ratio is remarkable, while in phase inversion zone, the effect of the mode of shaking is predominant in determination of emulsion type.

Now, we are confronted to the explanation of the mechanisms of shaking. Woodman,[13] in his experiments, attempted the explanation which, however, is complicated because adsorption, aging and partition between two phases of an emulsifying agent (gelatine) must be taken into account. In the present case, however, such disturbing factors due to the emulsifying agent are absent and mechanisms seem to be more simple.

In the case of shaking described in (1) of section (III), the lower part of a test tube is fixed and the upper portion of it is swung. Accordingly, the upper layer in the tube is first thrown against the upper end of the tube by the action of centrifugal force, and then follows the lower layer. Thus, the upper layer is crushed into droplets by compression between wall and the lower layer in which it is dispersed. Repeated shaking in this manner, therefore, establishes O-in-W emulsion and subsequent ordinary shaking of up-and-down motion also favours to increase the degree of dispersion of above emulsion type. The mode of shaking described in later part of (1) of section (IV) can be considered to give the same effect as the above case.

In the case of shaking mentioned in (2) of section (III), the upper portion of the tube is fixed and the lower portion is made to swing. In this case, the lower layer is not stirred, as it is confined between the upper layer and wall of the tube, while the upper layer is agitated, especially strong at the free surface. The agitation is extended down to the interface of two layers, where the lower liquid is stirred up and is gradually dispersed into the upper one. W-in-O emulsion is, therefore, established as the shaking goes on, and subsequnt ordinary up-and-down shaking also increases the degree of dispersion of this emulsion type.

The question arises as to what type would the ordinary up-and-down shaking favour to produce when it is applied from the beginning. It will be discussed upon this point.

In Table 2, three systems, (a), (b) and (c) are all taken in the phase inversion zone, and so the mode of shaking described in (1) or (2) of section (IV) favours to produce O-in-W or W-in-O emulsion respectively, in these systems. In the case, however, where usual up-and-down shaking is applied from the beginning as described in (3) of section (IV), system (a) produces O-in-W emulsion, system (b) that of W-in-O type, and system (c) occasionally produces both types of them. Each of these emulsion types is considered to be more favourable, respectively, than the other possible type. In phase inversion zone, those systems which are situated near the region A, generally show the tendency

to produce emulsion of the similar type to that in the region A (W-in-O emulsion as in (b)), and those near the region B show the tendency of producing emulsion of the same type as that in the region B (O-in-W emulsion as in (a)), by up-and-down shaking. Between these systems of (a) and (b), it is possible to consider the existence of such a system as (c), namely, the system which occasionally shows the tendency to produce both types of emulsions by up-and-down shaking.

It can also be seen from this table, that the type of emulsion once determined by a certain mode of shaking, is hard to be invrted by another mode of shaking. For example, system (b) produces W-in-O emulsion by usual up-and-down shaking, but when O-in-W emulsion is once established by the mode of shaking described in (1) of section (IV), subsequent up-and-down shaking only favours to increase the degree of dispersion of O-in-W type.

It is suggested in the eariier part of this section, that the distinction must be made between the tendency in establishment of emulsion type and the stability. Now, confirmations are made upon this point in Table 2. In the system (a), O-in-W emulsion is favourable to be produced in preference to W-in-O emulsion by usual mode of shaking, although emulsion of the latter type once produced is far more stable than that of the former, as shown in Table 2.

The general differences in behaviour or appearance between O-in-W and W-in-O emulsions are summarised in Table 3. It is said,[14] that

Table 3.

O-in-W emulsion	W-in-O emulsion
Produced by shaking of the mode (1)	Produced by shaking of the mode (2)
Emulsion drop moves upwards. Oily layer is separated upon the bulk (Fig. 2). Emulsion is comparatively unstable.	Emulsion drop sinks. Aqueous layer is separated at the bottom (Fig. 3). Emulsion is comparatively stable.
System does not foam. Bubble-in-drop system occurs frequently.	Foamy system occurs frequently.

there exists difference in stability between two possible types of drops formed at the interface separating two liquids. The present experiment shows it quantitatively.

Last of all, the explanation must be made upon the foam formation of the system shown in section (I). It is called for convenience sake foam-nonfoam system. Existence of such system is restricted in the region which forms a portion of phase inversion zone and at the same time forms a portion of foamy region of heterogeneous system of AEW.

(14) Rehbinder and Wenström, *Kolloid-Z.*, **53** (1930), 145.

In Fig. 6, A′ surrounded by dotted line, shows the foamy region[1] and hatching indicates the region of foam-nonfoam system.

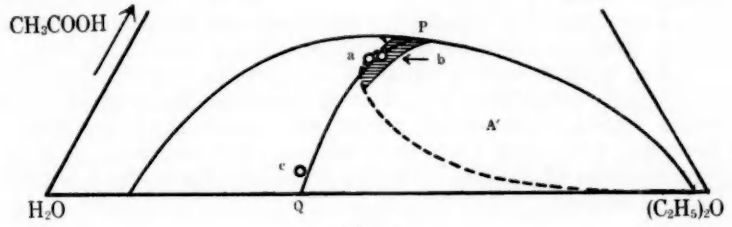


Fig. 6.

When we shake a system belonging to this region (system (a) or (b)), both types of emulsions are occasionally produced. In the case of O-in-W emulsion, bubbles which are produced at the same time in aqueous medium by shaking, are destroyed by emulsion droplets having smaller surface tension than that of dispersing medium, and no foam can be produced. In the case of W-in-O emulsion, on the other hand, emulsion droplets having larger surface tension than that of dispersing medium neither break bubbles, nor interfere with the foam formation of the system. These behaviours were schematically explained in the preceding report.[1] Accordingly, the above systems do not foam by shaking of the mode (1), while they can foam by shaking of the mode (2) of section (IV).

In the case of the system (c), the conditions are different. This system also belongs to phase inversion zone, but it is distant from the foamy region A′. So the system does not foam even when it forms W-in-O emulsion by shaking of the mode (2), while it produces emulsion droplets containing air bubbles, when it forms O-in-W emulsion by shaking of the mode (1) of section (IV), owing to the marked difference in surface tension between two phases.[1]

In foam-nonfoam system, therefore, the emulsion type is most readily confirmed by the presence or absence of the foam formation immediately after shaking. If the type of emulsion is inverted by some accident during the shaking, sharp change in foam formation can be observed. Thus, in a foam-nonfoam system which shows strong tendency to establish non foamy emulsion, foam formation can be seen so far as it is carefully shaken by the mode (2). It, however, turns suddenly into non foamy system, when it is shaken too strongly.

In conclusion, the author wishes to express his hearty thanks to Prof. J. Sameshima for his kind guidance. The expense for the experiments has been defrayed from a grant given to Prof. Sameshima by Nippon Gakujutsu Shinkokwai) (Japan Society for the Promotion of Scientific Research), to which the author's thanks are due.

Summary.

(1) It has been discovered, that there is certain heterogeneous system consisting of acetic acid, ethyl ether and water, which behaves

both foamy and non foamy, according to the different modes of shaking. This behaviour in foam formation is due to the difference in the type of emulsions produced.

(2) Three modes of shaking were noted and their influences upon the type of emulsion have been discussed.

(3) The heterogeneous region of this system is divided into three parts, according to the type of emulsion produced by shaking, namely, oil-in-water region, water-in-oil region and phase inversion zone. In phase inversion zone, both types of emulsions are possible to be produced by different modes of shaking. Observations and discussions were made upon these emulsions.

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The Electrolytic Formation of Persulphate. Part V. With Alternating Current Superimposed on Direct Current.

By Ryoichi MATSUDA and Teruichi NISHIMORI.

(Received February 21, 1939.)

The previous parts[1] of the present investigation dealt with the mechanism of persulphate formation and various influences of experimental conditions, when sulphate solutions were electrolysed with D.C. It was shown that the current efficiency, which will be denoted as C.E. hereafter, of electrolyses of sulphate solutions without diaphragm did not seem inferior to those of electrolyses with the same, so it could be assumed therefrom that cathodic reduction did not take place to any considerable extent in those cases. If it is the case, it cannot be expected that the C.E. will be improved by such a means as suppressing the cathodic reduction, but it is possible that the anodic oxidation will be influenced, favourably or unfavourably, when A.C. is superimposed upon D.C.

Various treatments of the Pt-anode prior to electrolysis caused more or less change in the C.E.,[2] and the best result was obtained when the anode had been heated by passing A.C. through it. In the present case A.C. takes part in the electrolysis itself, so that the circumstances are evidently much more complicated.

Experimental. The anode consists of a spiral of Pt-wire which is 0.1 cm. in diameter and 30.5 cm. long. It is thoroughly ignited im-

(1) Parts I–IV, this Bulletin, **11** (1936), 1; **11** (1936), 650; **12** (1937), 331; **12** (1937), 425 respectively.
(2) Part III, *ibid.*, **12** (1937), 331.

mediately before use and is kept rotating during electrolysis. The cathode consists of a Pt-plate, 5 cm. × 2.5 cm. The volume of electrolyte, unless specified, is 130 c.c. and it is electrolysed at 15°C. with the same amount of electricity by D.C., 3397 coulombs. A.C. which is of 60 cycles and 100 volts is superimposed upon it. The connection is as shown by Dr. Tanaka.[3] The analysis of the electrolysed solution is made by the same methods as those described in Part I. The C.E. is calculated with regard to D.C. only.

Experiment 1. 10 N sulphuric acid is electrolysed and the volume of the electrolyte is varied from 130 to 490 c.c. The C.E. are shown in Table 1 and Fig. 1 which are all referred to the total C.E. Those regarding to Caro's acid are always found less than 1% in these cases and are not shown here. The current density which is abbreviated as C.D. is referred to D. C. only.

Table 1. The C.E. of electrolysis of 10 N H_2SO_4. With 0.1 amp. A.C. superimposed on D.C.

C.D. (amp./dm².) / Volume of electrolyte (c.c.)	10	20	40	60	80
130	0.2%	0.3	6.2	14.1	24.5
195	14.9	15.7	19.9	—	27.9
260	8.3	13.3	23.0	—	47.4
325	0.9	3.0	13.0	—	28.7
490	0.7	1.3	5.5	—	19.8

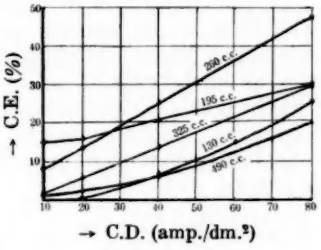

Fig. 1.

Experiment 2. 10 N sulphuric acid is electrolysed with diaphragm. Two different porcelain cylinders are used as diaphragm, one 38 mm. and the other 55 mm. in diameter. The anode is kept rotating at the center of the cylinder, and the solution inside it becomes the anolyte. With the smaller diaphragm, the anolyte is 45 c.c. and the catholyte 85 c.c.; with the bigger one, the anolyte 100 c.c. and the catholyte 30 c.c.

The catholyte is found not to contain peroxidic products. Therefore the C.E. shown in Table 2 and Fig. 2 are the results obtained by analysis of the anolyte. The C.E. of the electrolysis without diaphragm described in Experiment 1 is also shown in the figure for comparison. It is interesting to observe that when diaphragm is used the anodic oxidation takes place even with smaller C.D., while without diaphragm no, or very little, C.E. is obtained and also that the C.E. fluctuates little as the C.D. changes, when diaphragm is employed.

As stated already in the previous parts, the C.E. was not influenced much by the use of diaphragm when electrolysis was performed with D.C. only. It is observed in this case that the dimensions of diaphragm

(3) *J. Electrochem. Assoc. Japan*, **4** (1936), 4.

do not influence the C.E. considerably, although the greater cylinder is rather more favourable.

Table 2. The C.E. of electrolysis of 10 N H_2SO_4. With 0.1 amp. A.C. superimposed on D.C.

	C.D. (amp./dm^2.)	10	20	40	80
Diaphr. dia. 38 mm.	The total C.E.	16.3%	18.1	18.8	15.9
	The Caro's acid C.E.	0.3	0.2	0.1	trace
Diaphr. dia. 55 mm.	The total C.E.	13.8	16.6	19.2	16.6
	The Caro's acid C.E.	2.8	1.6	0.4	0.4

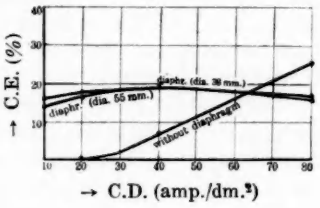

Fig. 2.

Experiment 3. Sulphuric acid containing a small quantity of potassium sulphate is electrolysed. The results are shown in Table 3 and Fig. 3. It can be seen that the C.E. is somewhat improved by replacing part of sulphuric acid with the sulphate when the present case and Experiments 1 and 2 are compared. In the electrolysis with diaphragm, the catholyte is found, in this case also, to contain no peroxidic products. The presence of diaphragm improves the C.E. at smaller C.D., and the bigger diaphragm is more favourable to the C.E., as in Experiment 2.

Table 3. The C.E. of electrolysis of H_2SO_4 containing K_2SO_4. With 0.1 amp. A.C. superimposed on D.C.

	C.D. (amp./dm^2.)	10	20	40	80
0.65N K_2SO_4 9N H_2SO_4	Without diaphragm	3.4%	8.3	21.8	39.5
0.64N K_2SO_4 9.36N H_2SO_4	With diaphragm (dia. 38 mm.)	18.1	13.5	19.0	49.3
0.64N K_2SO_4 9.36N H_2SO_4	With diaphragm (dia. 55 mm.)	20.3	27.4	32.7	40.5

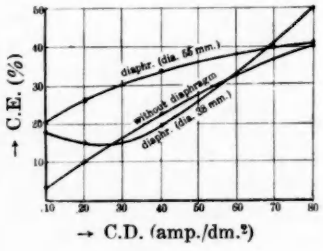

Fig. 3.

Experiment 4. A solution which is 0.64 N and 9.36 N respectively as regard to sodium sulphate and sulphuric acid is electrolysed. As in Experiment 3, the bigger diaphragm is more favourable to the C.E. than the smaller, but the difference is small. It is seen from the present case in comparison with the previous case in which the potassium salt is employed that potassium sulphate is more favourable in increasing the C.E. of persulphate formation than sodium sulphate. Such a difference between two sulphates is attributed to that Na-ions[4] are more effective catalysor to decompose persulphate than K-ions, as stated in Part I.

(4) A. Kailan and E. Leisek, *Monatsh.*, **50** (1928), 403.

Caro's acid is found less than 1% in C.E. in each electrolysis. The results are shown in Table 4 and Fig. 4.

Table 4. The C.E. of a solution which is 0.64 N Na_2SO_4 and 9.36 N H_2SO_4. With 0.1 amp. A.C. superimposed on D.C.

C.D. (amp./dm².)	10	20	40	80
Without diaphragm	3.4%	6.8	14.9	23.6
With diaphragm (dia. 38 mm.)	3.4	7.8	14.9	20.4
With diaphragm (dia. 55 mm.)	4.2	7.8	15.2	24.2

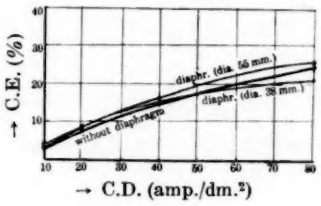

Fig. 4.

Experiment 5. The electrolyte is 0.64 N and 9.36 N with regard to ammonium sulphate and sulphuric acid respectively. The C.E. which is shown in Table 5 and Fig. 5 is nearly similar to that of Experiment 3 in which potassium sulphate is used, but is better than that of Experiment 4 in which the sodium salt is employed.

Table 5. The C.E. of a solution which is 0.64 N $(NH_4)_2SO_4$ and 9.36 N H_2SO_4. With 0.1 amp. A.C. superimosed on D.C.

C.D. (amp./dm².)	10	20	40	80
Without diaphragm	13.3%	17.6	25.9	40.1
With diaphragm (dia. 38 mm.)	11.3	18.9	23.2	33.1
With diaphragm (dia. 55 mm.)	16.7	22.5	32.0	48.3

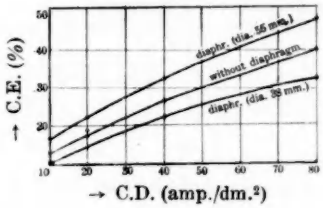

Fig. 5.

Experiments 6, 7, and 8. Three solutions which are 2 N and 8 N, 4 N and 6 N, and 6 N and 4 N as to ammonium sulphate and sulphuric acid respectively are electrolysed in these experiments. The more concentrated as to the sulphate the solution is, the greater is the C.E. But the present C.E. are inferior to those of corresponding cases described in Part I in which D.C. only took part. Therefore A.C. is not favourable to increase the C.E. of persulphate formation. The formation of Caro's acid in these cases is less than 1% in C.E. The results are shown in Table 6 and Fig. 6, 7, and 8.

Experiments 9 and 10. A solution which is 2 N ammonium sulphate and 8 N sulphuric acid, the same one as in Experiment 5, is electrolysed, but in the present case the quantity of A.C. is varied, the other conditions remaining the same. The influence of the amount of A.C. on the C.E. in these cases is not considerable. The results are shown in Table 7 and Fig. 9 and 10.

Table 6. The C.E. of electrolyses of solutions which contain $(NH_4)_2SO_4$ and H_2SO_4. With 0.1 amp. A.C. superimposed on D.C.

	C.D. (amp./dm^2.)	10	20	40	80
2N $(NH_4)_2SO_4$ 8N H_2SO_4	Without diaphragm	21.9%	26.7	42.3	50.3
	With diaphragm (dia. 38 mm.)	18.1	20.3	29.0	43.8
	With diaphragm (dia. 55 mm.)	18.5	26.4	39.7	48.1
4N $(NH_4)_2SO_4$ 6N H_2SO_4	Without diaphragm	26.8	37.4	52.1	54.5
	With diaphragm (dia. 38 mm.)	25.4	31.6	44.0	49.0
	With diaphragm (dia. 55 mm.)	29.6	40.3	53.5	61.8
6N $(NH_4)_2SO_4$ 4N H_2SO_4	Without diaphragm	37.9	46.4	60.0	64.0
	With diaphragm (dia. 38 mm.)	36.5	50.5	57.8	63.6
	With diaphragm (dia. 55 mm.)	37.3	50.8	62.5	65.5

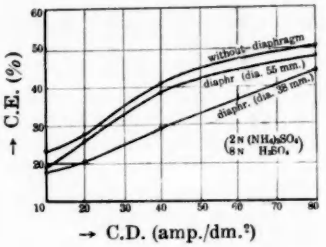

Fig. 6.

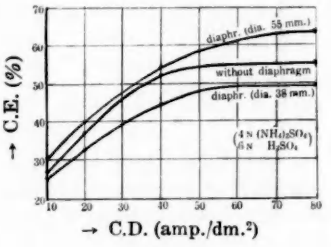

Fig. 7.

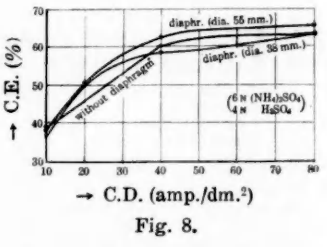

Fig. 8.

Table 7. The C.E. of electrolyses of a solution which is 2 and 8 N as to $(NH_4)_2SO_4$ and H_2SO_4 respectively. A.C. is superimposed upon D.C.

	C.D. (amp./dm^2.)	10	20	40	80
A.C. 0.01 amp.	Without diaphragm	15.6%	22.5	39.3	46.8
	With diaphragm (dia. 38 mm.)	15.1	21.8	39.4	44.9
	With diaphragm (dia. 55 mm.)	20.2	27.8	38.0	41.2
A.C. 0.2 amp.	Without diaphragm	10.5	32.0	41.2	44.6
	With diaphragm (dia. 38 mm.)	22.2	34.5	42.3	45.0
	With diaphragm (dia. 55 mm.)	27.8	36.7	43.3	45.8

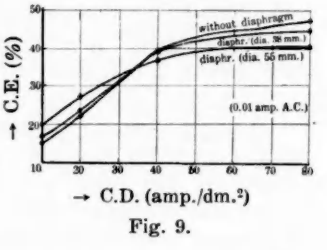

Fig. 9.

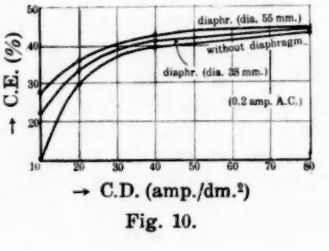

Fig. 10.

Experiment 11. 15 N sulphuric acid is electrolysed at 15°C. without diaphragm for 5 hours. The C.D. is 30 amp./dm.^{2} as to D.C., and A.C. is 0.1 amp. The same solution was electrolysed, with D.C. only, in Experiment 5 of Part II. In the latter case the Caro's acid C.E. fell off as the time went on, but in the present case it is kept nearly constant during the course of electrolysis. The total C.E. is almost the same in these two cases, falling off gradually with time. The results are shown in Table 8 and Fig. 11.

Table 8. The C.E. of electrolysis of 15 N H_2SO_4 without diaphragm. C.D. is 30 amp./dm^2. by D.C., and A.C. is superimposed on D.C.

Time (hour)	1	2	3	5
The total C.E.	60.7%	57.1	49.6	28.6
The Caro's acid C.E.	15 3	18.5	17.8	17.7

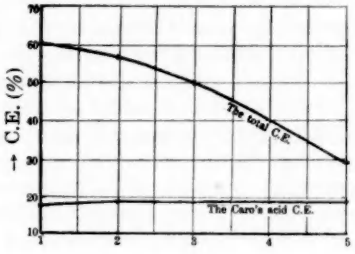

Fig. 11.

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Austauschreaktion der Sauerstoffatome zwischen einigen anorganischen Anionen und Wasser.[1]

Von **Toshizo TITANI** und **Kokiti GOTO.**

(Eingegangen am 27. Februar 1939.)

Inhaltsübersicht. Die Austauschreaktion der O-Atome zwischen einigen anorganischen Anionen, d.h. K_2SO_4, KNO_3, $NaClO_3$, K_2CO_3, KH_2AsO_4, KH_2PO_4 und $KHSO_4$, und Wasser in neutraler, alkalischer sowie saurer Lösung wird untersucht. Daraufhin kommen wir zu dem Schluss, dass die Reaktion nicht nur durch OH'-Ionen sondern auch durch H'-Ionen katalysiert wird. Als Mechanismus der Reaktion scheint uns in erster Linie der der Verseifung des organischen Esters am naheliegendsten in Betracht zu kommen. Aber für die Reaktion in saurer Lösung und besonders bei erhöhten Temperaturen können wir auch nicht ausser Acht lassen, dass die Austauschreaktion durch die Zwischenbildung der Anhydridmoleküle der betreffenden Säuren herbeigeführt wird.

Einleitung. Die Untersuchung der Austauschreaktion der O-Atome zwischen verschiedenen Arten der Anionen und Wasser ist insofern von

(1) Vorläufig mitgeteilt in diesem Bulletin, **13** (1938), 667.

Interesse als sie über das Verhalten der in Rede stehenden Anionen in wässrigen Lösungen einiges Licht werfen kann. Aus diesem Grunde haben wir die vorliegenden Versuche ausgeführt. Aber während dieser Zeit wurde dieselbe Aufgabe auch von anderer Seite aufgenommen, von der bereits einige interessante Ergebnisse vorliegen. Blumenthal und Herbert[2] fanden z.B., dass Kaliumphosphat K_3PO_4 seine ganzen vier O-Atome leicht gegen die des Wassers austauscht. Nach dem Versuch von Ingold und seinen Mitarbeitern[3] wurde ferner gefunden, dass die sämtlichen O-Atome des Natriumsulfats Na_2SO_4 in der mit Alkali versetzten Lösung gegen die des Wassers schnell ausgetauscht wird. Da aber die von Blumenthal und Herbert untersuchte Lösung von Kaliumphosphat in Wasser wegen der hydrolytischen Spaltung des Salzes ohne jeden Zusatz schon von selbst alkalisch reagiert, können wir die von allen diesen Autoren gewonnenen Ergebnisse kurz so zusammenfassen, dass die Austauschreaktion der O-Atome der anorganischen Anionen durch OH'-Ionen katalysiert wird. Nach unserem eigenen Versuch ergibt sich aber, dass diese Reaktion nicht nur durch OH'-Ionen sondern auch durch H'-Ionen katalysiert wird. Wir kamen zu dieser Annahme durch die Versuche, die mit den Lösungen von (i) K_2SO_4, KNO_3, $NaClO_3$; (ii) K_2CO_3; und (iii) KH_2AsO_4, KH_2PO_4, $KHSO_4$ sowie mit dem Gemisch von $K_2SO_4 + KHSO_4$, $KNO_3 + KHSO_4$, $NaClO_3 + KHSO_4$, $K_2SO_4 + HCl$ und $NaClO_3 + HCl$ ausgeführt wurden. Die Lösung der ersten dieser Gruppen reagiert offensichtlich neutral, die der zweiten alkalisch und die der letzten dritten sauer. Die messbar schnell verlaufende Austauschreaktion wird aber nur bei diesen beiden letzten Gruppen gefunden. Dagegen bei der ersten Gruppe, d.h. in neutraler Lösung, ist die Reaktion sogar bei ziemlich erhöhten Temperaturen kaum zu bemerken.

Versuchsanordnung. Eine abgewogene Menge des betreffenden Salzes wird in eine ebenfalls gut abgewogene Menge des an schwerem Sauerstoff angereicherten Wassers aufgelöst und die so hergestellte homogene Lösung wird in einem zugeschmolzenen Glasrohr bei einer bestimmten Temperatur, d.h. bei Zimmertemperatur, bei 100°C. bzw. bei 180°C., während einer gemessenen Zeitdauer stehen gelassen. Als Thermostat benutzten wir bei 100°C. das siedende Wasserbad, und bei 180°C. das elektrisch geheizte Luftbad. Nach der Erwärmung wird das Wasser durch die Destillation im Vakuum vom Salz abgeschieden und nötigenfalls wieder mit einer abgewogenen Menge des Salzes versetzt und erwärmt. Diese letzte Massnahmsregel ist oft nötig, wenn die Löslichkeit des betreffenden Salzes in Wasser bei der in Rede stehenden Temperatur nicht genügend gross ist. Nötigenfalls wiederholen wir deshalb denselben Prozess unter Verwendung immer desselben schweren Wassers einige Mal nacheinander, um die benötigte Menge des Salzes mit der angegebenen Menge des schweren Wassers restlos reagieren zu lassen. Eine einfache Rechnung zeigt,[4] dass die Veränderung der Dichte des schweren Wassers, die bei dieser Arbeitsweise durch die nacheinander folgend durch-

(2) E. Blumenthal und J.B.M. Herbert, *Trans. Faraday Soc.*, **33** (1937), 849.
(3) S.C. Datta, J.N.E. Day und C.K. Ingold, *J. Chem. Soc.*, **1937**, 1968.
(4) Vgl. dazu T. Titani und N. Morita, dies Bulletin, **13** (1938), 409.

geführte Destillation eventuell hervorgerufen wird, wohl ausser Acht gelassen werden darf. Wenn auf diese Weise der ganze Austauschversuch beendigt worden ist, wird das vom Salz abgeschiedene Wasser wie üblich sorgfältig gereinigt und dessen Dichteüberschuss dem gewöhnlichen Wasser gegenüber mittels eines Quarzschwimmers genau gemessen. Anderseits berechnen wir mit Hilfe der verwendeten Menge des Salzes und schweren Wassers sowie dessen Gehaltes an schwerem Sauerstoff vor dem Versuch den theoretisch erwartenden Wert der Dichteabnahme des benutzten schweren Wassers, die sich beim vollständigen Austausch ergeben würde. Wir können deshalb durch den Vergleich des so berechneten Wertes der Dichteabnahme des schweren Wassers mit dem experimentell gefundenen über den Austausch der O-Atome der in Rede stehenden Anionen zu einem Schluss kommen.

Die Ergebnisse der so ausgeführten Versuche sind in den weiter unten angegebenen Tabellen zusammengestellt. Aber bevor wir auf diese eingehen, möchten wir noch einige Worte über die Bereitung bzw. Vorbehandlung der zum Versuch verwendeten Salze sowie des schweren Wassers sagen. Die zu vorliegenden Versuchen benutzten Salze alle enthalten kein Kristallisationswasser. Aber sicherheitshalber werden sie immer direkt vor dem Versuch sorgfältig getrocknet, indem wir sie im Vakuum bei einer geeigneten Temperatur genügend lang erwärmen. Dabei geben wir für die wasserstoffhaltigen primären Salze wie z.B. KH_2PO_4 und KH_2AsO_4 besonders darauf Acht, dass keine wirkliche Entwässerung stattfindet. Die wirklich benutzte Trocknungstemperatur sowie die Trocknungsdauer geben wir oberhalb jeder Tabelle in den Klammern nach der chemischen Formel des betreffenden Salzes an. Das Kaliumsulfat wird z.B. durch die fünfstündige Erwärmung im Vakuum bei ca. 200°C. getrocknet. Das zum Versuch benutzte, an schwerem Sauerstoff angereicherte schwere Wasser wird durch die fraktionierte Destillation des gewöhnlichen Wassers bereitet. Deshalb ist es nicht nur an schwerem Sauerstoff sondern auch an schwerem Wasserstoff bis zu einem gewissen Grad angereichert. Die oberhalb jeder Tabelle angegebene Anzahl Δs_a zeigt den gesamten Dichteüberschuss des benutzten schweren Wassers vor dem Versuch. Von diesem gesamten anfänglichen Dichteüberschuss Δs_a ist aber der Betrag $\Delta s_a(O)$, ebenfalls oberhalb jeder Tabelle angegeben, auf die Anreicherung der schweren Sauerstoffisotope zurückzuführen. Da aber Δs_a durchschnittlich 35 bis 40 γ und $\Delta s_a(O)$ 23 bis 26 γ beträgt, ist der Gehalt des von uns benutzten schweren Wassers an schwerem Sauerstoff im Vergleich mit den von anderen Autoren benutzten verhältnissmässig klein. Jedoch weil wir erstens mit diesem Wasser bei jedem Versuch ziemlich reichlich verfuhren und zweitens der Dichteüberschuss des schweren Wassers mittels Quarzschwimmers bis unter $\pm 0.5\ \gamma$ genau gemessen werden konnte, dürfen die damit gewonnenen Ergebnisse wohl als genügend genau angesehen werden.

Versuche in neutraler Lösung. Die Austauschreaktion in neutraler Lösung kann nur äusserst schwer stattfinden, wie die folgenden drei Versuche mit K_2SO_4, KNO_3 und $NaClO_3$ zeigen.

Versuch 1. Kaliumsulfat.

K_2SO_4(200°C., 5 Stdn.), $\Delta s_a = 35.5\ \gamma$ und $\Delta s_a(O) = 23.1\ \gamma$ bei Zimmertemp., dagegen $\Delta s_a = 41.6\ \gamma$ und $\Delta s_a(O) = 26.1\ \gamma$ bei 100° und 180°C.

Versuchstemp. °C.	Versuchsdauer in Stdn.	K_2SO_4 in g.	H_2O in g.	Dichteabnahme in γ		Anzahl der Teilversuche
				gef.	ber.	
Zimmertemp.	72	28.0	20.0	1.2	9.5	14
100	20	25.0	20.0	0.8	8.8	6
180	100	21.0	20.0	2.1	7.9	4

Versuch 2. Kaliumnitrat.

KNO_3(240°C., 6 Stdn.), $\Delta s_a = 35.5\ \gamma$ und $\Delta s_a(O) = 23.1\ \gamma$ bei Zimmertemp., 80° und 100°C., dagegen $\Delta s_a = 41.6\ \gamma$ und $\Delta s_a(O) = 26.1\ \gamma$ bei 180°C.

Versuchstemp. °C.	Versuchsdauer in Stdn.	KNO_3 in g.	H_2O in g.	Dichteabnahme in γ		Anzahl der Teilversuche
				gef.	ber.	
Zimmertemp.	72	36.0	20.0	1.7	11.4	5
80	72	25.2	20.0	1.1	9.3	2
100	72	25.0	20.0	1.0	9.3	1
180	100	38.0	20.0	1.3	13.2	1

Versuch 3. Natriumchlorat.

$NaClO_3$(200°C., 8 Stdn.), $\Delta s_a = 41.6\ \gamma$ und $\Delta s_a(O) = 26.1\ \gamma$.

Versuchstemp. °C.	Versuchsdauer in Stdn.	$NaClO_3$ in g.	H_2O in g.	Dichteabnahme in γ		Anzahl der Teilversuche
				gef.	ber.	
100	10	40.0	20.0	1.3	13.2	1

Versuche in alkalischer Lösung. Dieser Versuch wird in der vorliegenden Arbeit nur mit der Lösung des Kaliumcarbonats durchgeführt, weil die katalytische Wirkung der OH'-Ionen schon durch die Versuche von den anderen Autoren als einwandfrei nachgewiesen wurde.[2][3]

Versuch 4. Kaliumcarbonat.

K_2CO_3(200°C., 5 Stdn.), $\Delta s_a = 35.5\ \gamma$ und $\Delta s_a(O) = 22.6\ \gamma$ bei Zimmertemp., dagegen $\Delta s_a = 41.6\ \gamma$ und $\Delta s_a(O) = 26.1\ \gamma$ bei 100° und 180°C.

Versuchstemp. °C.	Versuchsdauer in Stdn.	K_2CO_3 in g.	H_2O in g.	Dichteabnahme in γ		Anzahl der Teilversuche
				gef.	ber.	
Zimmertemp.[5]	72	45.0	20.0	0.2	9.3	3
100	30	40.0	20.0	11.1	11.5	1
180	5	40.0	20.0	10.7	11.5	1

(5) Vgl. auch T. Titani, N. Morita und K. Goto, dies Bulletin, **13** (1938), 329.

Versuche in saurer Lösung. Diese Versuche werden zunächst mit den Lösungen einiger saurer Salze und dann mit den der neutralen Salze, die aber durch den Zusatz des Kaliumbisulfats $KHSO_4$ bzw. konzentrierter Salzsäure HCl angesauert ist, ausgeführt. In den beiden Fällen geht die Austauschreaktion, besonders bei erhöhten Temperaturen, ziemlich schnell vor sich.

Versuch 5. Primäres Kaliumarsenat.

KH_2AsO_4(100°C., 10 Stdn.), $\Delta s_a = 41.6\ \gamma$ und $\Delta s_a(O) = 26.1\ \gamma$.

Versuchstemp.	Versuchsdauer in Stdn.	KH_2AsO_4 in g.	H_2O in g.	Dichteabnahme in γ		Anzahl der Teilversuche
				gef.	ber.	
Zimmertemp	70	27.0	10.0	17.0	16.9	1
„	70	27.0	10.0	16.2	16.9	1

Versuch 6. Primäres Kaliumphosphat.

KH_2PO_4(150°C., 6 Stdn.), $\Delta s_a = 41.6\ \gamma$ und $\Delta s_a(O) = 26.1\ \gamma$.

Versuchstemp. °C.	Versuchsdauer in Stdn.	KH_2PO_4 in g.	H_2O in g.	Dichteabnahme in γ		Anzahl der Teilversuche
				gef.	ber.	
Zimmertemp.	20	28.5	20.0	4.6	13.7	3
100	100	30.0	20.0	13.0	14.1	1

Versuch 7. Kaliumbisulfat.

$KHSO_4$(150°C., 8 Stdn.), $\Delta s_a = 41.6\ \gamma$ und $\Delta s_a(O) = 26.1\ \gamma$.

Versuchstemp. °C.	Versuchsdauer in Stdn.	$KHSO_4$ in g.	H_2O in g.	Dichteabnahme in γ		Anzahl der Teilversuche
				gef.	ber.	
Zimmertemp.	20	30.0	20.0	6.0	12.9	3
100	20	24.0	20.0	10.8	11.5	1
180	100	30.0	20.0	12.6	12.9	1

Versuch 8. Kaliumsulfat+Kaliumbisulfat.

Die beiden Salze werden genau so wie beim Versuch 1 bzw. 7 vorbehandelt. $\Delta s_a = 41.6\ \gamma$ und $\Delta s_a(O) = 26.1\ \gamma$.

Versuchstemp. °C.	Versuchsdauer in Stdn.	K_2SO_4 in g.	$KHSO_4$ in g.	H_2O in g.	Dichteabnahme in γ		Anzahl der Teilversuche
					gef.	ber.	
100	20	20.0	4.0	20.0	2.0	9.3	4
100	20	30.0	2.4	20.0	2.7	10.8	6
180	20	23.5	6.75	20.0	9.5	11.0	5
180	20	22.0	2.4	20.0	8.5	9.3	4

Versuch 9. Kaliumnitrat+Kaliumbisulfat.

Die beiden Salze werden genau so wie beim Versuch 2 bzw. 7 vorbehandelt. $\Delta s_a = 41.6\ \gamma$ und $\Delta s_a(O) = 26.1\ \gamma$.

Versuchstemp. °C.	Versuchsdauer in Stdn.	KNO_3 in g.	$KHSO_4$ in g.	H_2O in g.	Dichteabnahme in γ		Anzahl der Teilversuche
					gef.	ber.	
180	20	15.0	3.0	20.0	—	8.4	1

Bei diesem Versuch bemerkten wir, dass die Lösung sich während der Erwärmung allmählich schwach bräunlich gelb färbte und zugleich ein rotbrauner Dampf entwickelt wurde, der aber nicht entweichen konnte, da die Lösung wie üblich in einem zugeschmolzenen Glasrohr erwärmt wurde. Diese Färbung der Lösung sowie der Dampfphase blieb aber sogar noch nach der Erkaltung der Röhre zurück, obwohl in viel geringerem Masse als während der Erwärmung, und die so verunreinigte Lösung erwies sich sehr schwer zu reinigen. Deshalb haben wir diesen Versuch unterbrochen.

Versuch 10. Natriumchlorat+Kaliumbisulfat.

Die beiden Salze werden genau so wie beim Versuch 3 bzw. 7 vorbehandelt. $\Delta s_a = 41.6\ \gamma$ und $\Delta s_a(O) = 26.1\ \gamma$.

Versuchstemp. °C.	Versuchsdauer in Stdn.	$NaClO_3$ in g.	$KHSO_4$ in g.	H_2O in g.	Dichteabnahme in γ		Anzahl der Teilversuche
					gef.	ber.	
100	10	33.0	6.0	20.0	12.9	13.4	1

Bei diesem Versuch bemerkten wir ähnlich wie beim vorhergehenden Versuch 9, dass die Lösung allmählich schwach gelb und die Dampfphase schwach gelblich braun während der Erwärmung gefärbt wurde und diese Färbung sogar nach der Erkaltung der Röhre, wenn auch in viel geringerem Masse als während der Erwärmung, zurückblieb. Aber weil das von dieser Lösung durch die Destillationen im Vakuum abgetrennte Wasser im Gegenteil zu dem vorhergehenden Versuch 9 mit KNO_3 ziemlich leicht gereinigt werden konnte, haben wir seinen Dichteüberschuss wie üblich bestimmt und fanden, dass die so gemessene Dichteabnahme des Wassers hinreichend gut mit dem berechneten Wert übereinstimmt, wie die obige Tabelle zeigt.

Versuch 11. Kaliumsulfat+Salzsäure.

Man lässt 5.0 g. gut getrocknetes Kaliumsulfat zusammen mit 0.15 c.c. 37 prozentiger Salzsäure in 20.0 g. schweres Wassers sich auflösen und die so hergestellte Lösung in einem zugeschmolzenen Glasrohr 20 bzw. 100 Stdn. lang bei 180°C. stehen. Dann wird das Wasser durch die Destillation im Vakuum vom zugesetzten Kaliumsulfat abgetrennt und die dabei

zusammen mit dem Wasser abdestillierte Salzsäure unter Zusatz einer minimalen Menge festen Ätzkalis neutralisiert. Das auf diese Weise vom Kaliumsulfat sowie von der Salzsäure abgeschiedene Wasser wird wieder mit 5.0 g. Kaliumsulfat und 0.15 c.c. Salzsäure versetzt und 20 bzw. 100 Stdn. lang bei 180°C. stehen gelassen. Nach viermaliger Behandlung ein und desselben schweren Wassers immer mit erneutem Salz und Säure wird es davon abgeschieden, richtig gereinigt und sein Dichteüberschuss genau gemessen.

K_2SO_4(200°C., 5 Stdn.), HCl(37%), $\Delta s_a = 41.6\ \gamma$ und $\Delta s_a(O) = 26.1\ \gamma$.

Versuchstemp. °C.	Versuchsdauer in Stdn.	K_2SO_4 in g.	HCl(37%) in c.c.	Dichteabnahme in γ		Anzahl der Teilversuche
				gef.	ber	
180	20	20.0	0.6	5.6	7.6	4
180	100	20.0	0.6	5.0	7.6	4

Versuch 12. Natriumchlorat + Salzsäure.

Der Versuch wird auf ähnliche Weise wie beim vorerwähnten Versuch 11 ausgeführt.

$NaClO_3$(200°C., 8 Stdn.), HCl(37%), $\Delta s_a = 41.6\ \gamma$ und $\Delta s_a(O) = 26.1\ \gamma$.

Versuchstemp. °C.	Versuchsdauer in Stdn.	NaClO in g.	HCl(37%) in c.c.	Dichteabnahme in γ		Anzahl der Teilversuche
				gef.	ber.	
100	10	25.0	0.15	5.2	10.0	1

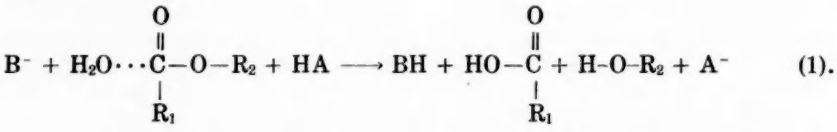
Bei diesem Versuch fanden wir ebenso wie beim Versuch 10 mit Natriumchlorat und Kaliumbisulfat aber in viel geringerem Masse als dabei, dass die Lösung sowie die Dampfphase während der Erwärmung schwach gelb gefärbt wurde.

Diskussion. Aus den oben angegebenen Versuchsergebnissen darf wohl geschlossen werden, dass die Austauschreaktion der O-Atome der anorganischen Anionen in wässriger Lösung nicht nur durch OH′-Ionen sondern auch durch H˙-Ionen katalysiert wird.[6] Die naheliegendste Annahme für den Mechanismus dieser Austauschreaktion ist deshalb, wie darauf schon von Herbert und Lauder[7] hingewiesen wurde, dass sie nach dem ähnlichen Mechanismus wie bei der Verseifung des organischen Esters in wässriger Lösung verläuft. Betreffend des Mechanismus der Verseifung des Esters, oder im allgemeinen solch einer Reaktion, die nicht nur durch H˙-Ionen sondern auch durch OH′-Ionen katalysiert wird, wird

(6) Die katalytische Wirkung der H˙- und OH′-Ionen auf die Austauschreaktion der O-Atome des Acetons in wässeriger Lösung wurde schon von M. Cohn und H.C. Urey (*J. Am. Chem. Soc.*, **60** (1938), 679 und *J. Chem. Phys.*, **6** (1938), 175) gefunden.

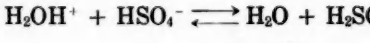
(7) J.B.M. Herbert und I. Lauder, *Trans. Faraday Soc.*, **34** (1938), 1219; *Nature*, **142** (1938), 954.

neuerdings eine Theorie von Horiuti und Sakamoto[8] aufgestellt. Danach muss der geschwindigkeitsbestimmende Prozess bei dieser Art der säure-basen-katalytischen Reaktion derart sein, dass ein Proton von einer Brönstedschen Säure zu einem Brückensauerstoffatom des Zwischenkomplexes bzw. Quasimoleküls angehäftet wird, das sich zwischen dem betreffenden Estermolekül und Wasser bildet, und zugleich ein Proton von diesem Zwischenkomplex zu einer Brönstedschen Base abgegeben wird. Das Estermolekül wird dabei durch die quantenmechanische Resonanz zwischen diesen beiden Prozessen in seine Bestandteile abgespaltet. Das Reaktionsschema kann nämlich folgendermassen ausgedrückt werden:

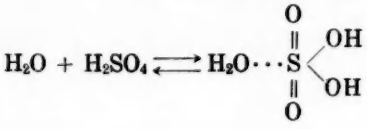


(1).

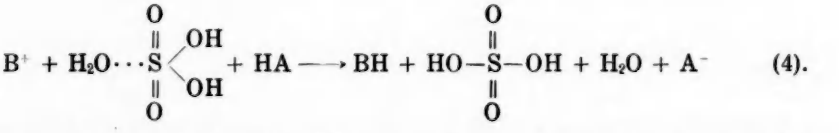
In dieser Formel bedeutet HA und B^- resp. die Brönstedsche Säure und Base und R_1 und R_2 ein organisches Radikal. Aber weil die in der vorliegenden Arbeit untersuchte Austauschreaktion der anorganischen Anionen ebenfalls durch H'- und OH'-Ionen katalysiert wird, liegt die Annahme nahe, dass diese Reaktion auch nach dem ähnlichen Mechanismus verläuft. Wir können z.B. die Austauschreaktion des Bisulfations etwa wie folgend formulieren:



(2),



(3),



(4).

Dem durch Reaktion (2) gebildete neutralen undissoziierten Säuremolekül wird bei der daraufolgenden Reaktion (3) ein Wassermolekül angelagert und ein Zwischenkomplex bzw. Quasimolekül gebildet. Diese beiden Reaktionen müssen aber sehr schnell verlaufen und folglich sich immer im Gleichgewicht halten. Beim letzten geschwindigkeitsbestimmenden Prozess (4) wird aber, ähnlich wie bei der Verseifung des Esters, ein Proton von einer Brönstedschen Säure HA an einem Hydroxylsauerstoffatom dieses Zwischenkomplexes angehäftet, zugleich ein Proton von diesem letzteren zu einer Brönstedschen Base B^- abgegeben und der Zwischenkomplex wieder im Säuremolekül und Wasser abgespaltet. Es ist ohne weiteres klar, dass die sämtlichen O-Atome des Säuremoleküls und folglich des betreffenden Anions durch die nacheinander folgende Zirkulation

(8) J. Horiuti und Y. Sakamoto, noch nicht veröffentlicht.

dieser drei Teilreaktionen (2) bis (4) allmählich gegen die des Wassers ausgetauscht werden.

Falls nun die Austauschreaktion der O-Atome der anorganischen Anionen wirklich nach dem oben angegebenen der Verseifung des organischen Esters ähnlichen Mechanismus stattfindet, dann kann es sehr aussichtsreich sein, die säurekatalysierte Austauschreaktion der O-Atome nicht nur in einem an schwerem Sauerstoff angereicherten Wasser, d.h. nicht nur in H_2O^{18}, sondern auch in einem an beigen Arten der schweren Isotope angereicherten Wasser, nämlich in D_2O^{18}, auszuführen und die Austauschgeschwindigkeit in beiden Fällen zu vergleichen. Aber bevor wir auf diese Frage eingehen, müssen wir noch eine andere Möglichkeit für den Mechanismus der Austauschreaktion in Erwägung ziehen. Nämlich, dass das durch die oben angegebene Reaktion (2) gebildete undissoziierte Säuremolekül reversibel in Anhydridmolekül und Wasser gespaltet wird, wie z.B.:

$$H_2SO_4 \rightleftarrows H_2O + SO_3 \qquad (5)$$

Wenn solch eine reversible Dissoziation des Säuremoleküls wirklich in der Lösung stattfindet, dann kann die Austauschreaktion offensichtlich auch dadurch herbeigeführt werden und diese letztere Möglichkeit können wir besonders bei den Versuchen in saurer Lösung und bei erhöhten Temperaturen nicht ausser Acht lassen. Wir haben tatsächlich bei den Versuchen in saurer Lösung mit solchen Anionen, die flüchtige Anhydridmoleküle bilden können, wie z.B. beim Versuch 9 mit Kaliumnitrat + Kaliumbisulfat, beim Versuch 10 mit Natriumchlorat + Kaliumbisulfat sowie beim Versuch 12 mit Natriumchlorat + Salzsäure, ein deutliches Anzeichen für die Bildung der Anhydridmoleküle der betreffenden Säuren und zugleich die ziemlich glatt verlaufende Austauschreaktion beobachten können. Aber augenblicklich ist es uns nicht möglich, zwischen diesen beiden Möglichkeiten so ohne weiteres einen Entscheid zu treffen, bis die Reaktion noch eingehender wie z.B. kinetisch untersucht wird. Jedoch allem Anschein nach möchten wir lieber annehmen, dass im allgemeinen die beiden Mechanismen gleichzeitig bzw. nebeneinander eine Rolle spielen. Diese Annahme liegt natürlich um so näher, wenn die Reaktion in saurer Lösung stattfindet. Aber auch wenn die Reaktion in alkalischer Lösung ausgeführt wird, lässt sich die Möglichkeit der Austauschreaktion durch die Anhydridbildung nicht ohne weiteres von der Hand weisen, falls die Alkalinität von der hydrolytischen Spaltung des in Rede stehenden Salzes selbst herbeigeführt wird, wie z.B. dies beim vorliegenden Versuch 4 mit Kaliumcarbonat der Fall ist.

Zum Schluss möchten wir der Nippon-Gakujutzu-Shinkohkai (der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Forschungen) sowie der Hattori-Hohkohkai (der Hattori-Stiftung) für ihre finanzielle Unterstützung bei der Ausführung der vorliegenden Arbeit unseren wärmsten Dank aussprechen.

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